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FRACTURE PROPERTIES OF POLYPHENYLENE OXIDE COMPOSITES

By

K. L. TRACHTE
A. T. DiBENEDETTO

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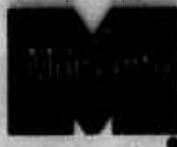
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A. T. DiBENEDETTO

NOVEMBER 1970

FOREWORD

The research reported herein was conducted by the staff
of the Monsanto/Washington University Association under the
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FRACTURE PROPERTIES OF POLYPHENYLENE OXIDE COMPOSITES

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ABSTRACT

The mechanical properties of glass bead, randomly oriented short glass fiber and randomly oriented short graphite fiber polyphenylene oxide composites were investigated. Fracture toughness measurements were made using double edge notched tensile specimens and tensile strength, tensile strain and initial elastic modulus were measured in standard ASTM tensile tests.

It was found that the fracture toughness was relatively independent of filler types and geometry (and nearly equal to that of the unfilled polymer) when no polymer-filler adhesion was present. When adhesion was promoted by surface treatment of the reinforcement, the fracture toughness of the treated fiber composites was greater than that of the untreated composites, while that of the treated particulate composites was below that of the untreated materials. The fracture toughness was also relatively independent of fiber concentration, but decreased sharply with increased glass bead concentration.

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The elastic moduli of the composites varied in a predictable fashion with temperature and reinforcement concentration. The ultimate tensile strength and the elongation at break were a sensitive function of interfacial adhesion and reinforcement geometry. The overall performance of the various systems was evaluated by considering the combined mechanical response of each system and rating them relative to one another.

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INTRODUCTION

All materials contain a distribution of inherent flaws
which act as sites for stress concentration. If a stress intensity
at one of the flaw tips is produced which is greater than the
material can withstand, the flaw begins to grow in size. At some
critical condition, the crack front becomes unstable and
propagates catastrophically through the remaining cross-section
of material.

Fillers, acting as stress concentrators, significantly
multiply the number of sites for potential crack growth. In
particular, when debonding of the polymer from the filler occurs,
a crack of rather substantial dimensions can result. Designing
against brittle fracture in composite materials is, therefore,
of prime importance.

Irwin has developed the concept of "fracture toughness" as
an index of the brittleness of a material. It is a measure of
the amount of energy required to catastrophically propagate a
crack through a brittle material (1,2,3,4). In this paper,
Irwin's isotropic fracture mechanics have been applied to

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"quasi-isotropic" filled systems by examining the plane strain fracture toughness of thermoplastic polyphenylene oxide polymers filled with a variety of reinforcing agents.

The fracture toughness γ of a material is defined as one-half the critical strain energy release rate G_c (i.e., $\gamma = G_c/2$). These parameters are related to Irwin's critical stress parameter, K_c, which is a measure of the stress intensity near the crack tip at the onset of catastrophic failure. For a plane strain fracture mode, $\gamma = K_c^2 (1-\nu^2)/2E$, where E is Young's modulus and ν is Poisson's ratio.

For a double edge notched specimen of the type shown in Figure 1, Irwin has shown that K_c is approximated by:

$$K_c = \sigma \left[W \, \tan \frac{\pi \left(a + r_y\right)}{W} + 0.1 \, \sin \frac{2\pi \left(a + r_y\right)}{W} \right]^{1/2} \quad (1)$$

where σ is the gross stress at break based on the original cross-section, W is the sample width, a is the half crack length at the point of catastrophic failure and r_y is a correction term which estimates the effect of plastic deformation in the vicinity of the crack tip on the stored elastic energy at the critical condition. The quantity r_y is referred to as the "plastic zone" and may be calculated from the equation:

$$r_y = \frac{1}{2\pi} \left(\frac{K_c}{\sigma_y}\right)^2 \quad (2)$$

where σ_y is the yield strength of the material. The half crack length, a, is equal to the initial machined half crack length a_o plus the length of the slow stable growth section prior to catastrophic crack propagation.

One may also define the fracture toughness, independent of any theoretical mechanics analysis, directly in terms of the change in compliance with crack length. Irwin has also shown (2) that:

$$\gamma = \left(P^2/4t\right)\left[\frac{\partial(\delta/P)}{\partial(2a)}\right]_P = \left(P^2/4t\right)\left[\frac{\partial\,1/M}{\partial(2a)}\right]_P \qquad (3)$$

where P is total load, δ is total deflection, M is the compliance P/δ, t is specimen thickness and 2a is the total crack length. Thus one may prepare a series of specimens with cracks of different size and from a plot of measured compliance versus initial crack length, determine a value for the fracture toughness.

With the materials studied in this work, the fracture toughnesses determined from experiments using a double edge notched sheet and calculated using Irwin's fracture mechanics (equation 1) were always the same, within experimental accuracy, to values determined from experiments on a series of prenotched specimens and calculated using equation 3. This indicates that Irwin's isotropic fracture mechanics was applicable to the "quasi-isotropic" materials used in this study.

EXPERIMENTAL

The following systems were investigated:

1) Unfilled polyphenylene oxide, PPO (General Electric, Grade 631-111).

2) A 10%, 20%, and 30% by volume glass microbead/PPO composite with and without A-1100 silane (γ-amino propyltriethoxysilane) coupling agent.

3) A 2%, 5%, 10%, 30%, and 45% by volume 1/8" length randomly dispersed E-glass fiber/PPO composite.

4) A 20% by volume 1/8" length randomly dispersed E-glass fiber/PPO composite with and without A-1100 silane coupling agent.

5) A 20% by volume 1/8" length randomly dispersed Thornel 40 graphite fiber/PPO composite.

A schematic drawing of the fracture toughness test specimen is shown in Figure 1. The initial edge cracks were machined using a flywheel cutter with a carbide tip. The edge slots were aligned to within ± 0.0025 centimeters of each other. Notch root radii of less than 0.002 cm were used in all cases. (At root radii of more than 0.01 cm the fracture toughness results are sensitive to the notch geometry). All samples were cut to $a_o = 0.508 \pm 0.0025$ cm, annealed and examined under polarized light to insure no residual stresses after machining. The test specimen was glued to steel plates using Eastman 910 adhesive.

The system was mounted in an Instron Testing Machine with alignment of the loading pins to better than 0.0025 cm. Pin loading at two holes on top and bottom of the plates, 4 cm from the adhesive joints, insured a uniform tensile load in the test section.

Yield strengths were obtained in a similar manner but the microtensile specimens were dimensioned to ASTM specification D 1708(5). Young's moduli were measured on 1.25 cm x 0.63 cm x 10 cm samples using Instron strain gage extensometers where temperature allowed, or directly from the force-deflection curves at higher temperatures.

The polyphenylene oxide was supplied as a 20 to 400 mesh powder and was dried at 125°C and 29.9 inches of vacuum for 8-10 hours prior to compression molding. All samples were carefully annealed after compression molding to minimize thermal stresses. The glass microbeads were from Cataphote Company and had a size range of 1-30 microns. Prior to use they had to be magnetically cleaned of iron particles present in the as-received material. The fiber glass was Johns-Manville 1/8 inch length E-glass, type CS-308A. Prior to use, the sizing was burned off in a muffle furnace at 600°C for 3 to 6 hours. The graphite fibers were Thornel 40 from Union Carbide Corporation. The continuous graphite fiber was chopped to 1/8 inch lengths and the short fiber bundles were refluxed with methanol in a Soxhlet Extractor for 24 hours to remove the polyvinyl alcohol sizing.

When required, the reinforcements were treated with A-1100 silane. The glass microbeads were treated with 1.54 cc A-1100 and

0.385 cc H_2O per 100 grams of beads in a benzene carrier and were heated and stirred at 40°C for 8 hours. The excess fluid was decanted and the treated beads were dried at 110°C and 29.9 inches of vacuum. The E-glass fibers were treated in the mixing operation (described below) by adding 1% A-1100 and 0.25% H_2O directly to the methanol carrier.

The most difficult step in the preparation of the composites was dispersing the fillers uniformly throughout the PPO matrix prior to the final compression molding. A technique of dry blending PPO powder of less than 200 mesh with the glass bead was used for the particulate composites. To obtain homogeneous dispersions of discontinuous fibers it was necessary to use a methanol carrier into which PPO powder and fibers were mixed. To minimize handling, a preform mat of the same size as the compression mold was prepared. The details of the procedure have been reported previously (6,7). These materials were found to be "quasi isotropic" by compliance tests (8,9,10) and three dimensionally random by photographic analysis.

It was evident from electron scanning microscope photographs of fracture surfaces that the application of A-1100 silane to the glass surfaces promoted a moderate adhesion between phases. The difference L ween untreated surfaces and treated ones is illustrated in Figures 2 and 3. Figure 2 shows that the resin pulls cleanly away from the bead surfaces and the beads merely sit in the center of large craters formed by the fracture front. With moderate adhesion, relatively few beads are at the surface and

those that are still have adhering resin. Similar differences
were observed with the E-glass fibers but we were not able to
promote adhesion to the graphite fiber surfaces. Although we
occasionally observed some fiber fracture, the primary mode of
failure for the ductile PPO matrix fiber composites was through
fiber pullout, after interfacial debonding.

In the fracture toughness calculations, one must know the
strength at the crack tip. This leads to a problem, as the
strain rate at the crack tip of the notched sample during testing
is likely much greater than that of the notched sample as a whole (11).
The effect of increasing strain rate on the ultimate or yield
strength of a polymer is well known (12-15). Regardless of this,
error analysis on the calculation of fracture toughness indicated
that strain rate effects for tensile strength are only important
beyond a 3 decade range (7). Therefore, yield and ultimate
strength data obtained from unnotched tensile samples at a strain
rate of 0.013/min were used for the crack tip tensile strength
in the fracture mechanics calculations.

In this paper yield strength, σ_y, is defined as the stress at
the maximum in the stress-strain curve. Ultimate strength, σ_u,
refers to the maximum stress achieved in a brittle system (i.e.,
the stress at fracture is the maximum stress).

The test rate of the notched sample was 0.25 $(min)^{-1}$. Test
temperature was varied from -50°C to the main glass temperature
of PPO at 210°C.

RESULTS

(a) Tensile Properties

The tensile strengths are shown in Figures 4, 5, and 6. The untreated glass bead/PPO composites and the unfilled PPO always exhibited a yield point in the stress-strain curve. Below 150°C all other composites failed before yielding, while above 150°C they also yielded.

As shown in Figure 4, introduction of glass beads into the PPO polymer resulted in a reduction of the tensile strength at all test temperatures. The strength reduction for the untreated glass bead composite varied from 35% at -50°C to 45% at 50°C. Treatment of the beads with A-1100 silane coupling agent increased the tensile strength, nearly back to the level of the unfilled PPO.

In contrast to the bead composites, the random glass fiber composites showed significant strengthening of the PPO polymer over the entire test temperature range. Even without polymer fiber interfacial adhesion, the tensile strength was increased by 30% at -50°C to 100% at 190°C. Addition of A-1100 silane treatment to the glass fibers increased the tensile strength of the composite another 20% to 50% over the same temperature range.

The graphite fiber composite tensile strength has a strikingly different dependence on temperature from that of the glass filled composites. For the glass composites, the slopes of the stress-temperature curves appear to be identical to that of the unfilled PPO. This is not true for the graphite fiber composite. At low temperatures the tensile strength was below that of the glass bead

composites, while at temperatures approaching the main glass temperature, the tensile strength equaled that of the glass fiber composites. It is expected that this strength difference may be due to the unusual anisotropy and cross-sectional geometry of Thornel fibers (7). To date, no definitive experimental program has been carried out to investigate these factors.

The yield strength of the untreated glass bead composites continually decreased with increasing filler concentration. The ultimate strength of the A-1100 treated glass bead composites at first decreased to about 15% by volume beads, then increased nearly back to the unfilled polymer strength at 25% by volume filler. These results are consistent with predictions for particulate filled systems, as presented by Nielsen (16).

The ultimate strength of the untreated glass fiber composite increased linearly to about 20% by volume fibers, then decreased slightly, as shown in Figure 6. Since the maximum theoretical volume loading for a random fiber system is of the order of 50% to 60%, the strength is expected to decrease sharply above 45% by volume fibers, as more and more void formation and adjacent fiber abrasion takes place. Lee (17) has reported data on twelve thermoplastic polymers reinforced with random short glass fibers that, in general, agree with the tensile results presented here.

The ultimate strains are shown in Figures 7 to 9. For all composites, the ultimate strain or yield strain was less than the yield strain of the unfilled PPO at the same temperature. The graphite fiber composite was the most brittle, whereas the untreated

glass bead composite showed the most ductility. Increasing the
filler concentration drastically decreased the ultimate and yield
strain attainable in all composites. The glass bead composite
strain data were consistent with Nielsen's prediction for a
particulate filled system (16).

Figure 10 shows the initial moduli as a function of temperature.
In all cases the moduli decreased slightly with increasing
temperature up to within 50°C of the main glass temperature. At
higher temperatures the moduli decreased rapidly toward approximately
zero at the glass temperature. The effect of filler content on
initial modulus is shown in Figure 11. The treated and untreated
glass bead composite had exactly the same initial elastic modulus.
This is probably the result of the compressive forces on the
glass bead reinforcement causing sufficient frictional resistance
at low deformation to mask the lack of adhesion between phases.
The moduli of the particulate filled composites follow Kerner's
equation (18) for modulus up to the volume fractions investigated.
The moduli of the A-1100 treated glass fiber, untreated glass fiber,
and graphite fiber composites fall between the random-on-a-plane
theory of Tsai (19) and that of Nielsen and Chen (20) or Lees (21).
It was expected that the data would be lower than these predictions
since the fiber composites were shown to be nearly three-dimensional
rather than random-on-a-plane. However, as seen, this was not the
case.

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(b) Fracture Toughness

The fracture toughness γ is shown in Figure 12 as a function of temperature. Rather than showing individual data points, the average 90% confidence band for each curve is shown on the left. The unfilled PPO exhibited a maximum in γ near 120°C while the measured values for the composites were relatively unaffected by temperature, up to about 120°C. Above this temperature, γ for the composites increased rapidly, in spite of the fact that the value for the unfilled polymer decreased sharply. These high temperature values of γ are probably spurious, since macroscopic yielding was observed at the notched cross-section above 150°C, thus invalidating the linear mechanics analysis. Presumably this yielding situation at the notched cross-section in the composite results from the fillers acting as stress concentrators. Above 120°C a sufficiently enlarged plastic zone occurs at both notches, enhancing the onset of yielding. In the unfilled PPO, γ decreased above 120°C, presumably due to easy local plastic flow at the crack tip. This flow process did not sufficiently enlarge the plastic zone to promote macroscopic yielding (7).

The addition of A-1100 treated glass beads to the polymer significantly reduced γ below that of the untreated bead composite, while A-1100 treated glass fibers caused the opposite effect relative to the untreated glass fiber composites. Moreover, untreated composites had approximately the same value of γ as the unfilled polymer, up to 120°C.

We conclude from this that, unlike the tensile properties, γ is relatively independent of filler type or geometry for a quasi-isotropic system when no polymer-filler adhesion is present. If adhesion is combined with an opportunity for stress transfer from the polymer matrix to the filler, as with the glass fibers, an increase in γ will result. If adhesion is present with little possibility of stress transfer from the polymer matrix to the filler, γ will decrease, because of the inhibition of the plastic flow near the filler surfaces (6).

The effect of filler content on fracture toughness is shown in Figure 13. The glass bead composite data discussed below has been previously reported (6,7), but it is presented again for comparison with the untreated glass fiber composite data.

Addition of glass beads to the polymer decreased the fracture toughness. With adhesion present, γ was reduced an additional 20 to 30% more than for the untreated glass bead composite. Nielsen (16) predicts that the modulus of toughness for particulate composites should be less when adhesion is present. The data also shows this is true for the fracture toughness.

The fracture toughness for the untreated glass fiber composite remained nearly constant to about 20% by volume fibers. Above 20% by volume, γ began to decrease. It is reasonable to expect that γ will approach zero between 50% to 70% by volume filler for these composites, where the maximum packing would be achieved.

Use of Irwin's fracture mechanics also provides an estimate of the plasticity at the crack tip at fracture. The effect of temperature on this "plastic zone," r_y is shown in Figure 14. As seen, there is considerable difference in crack tip plasticity at fracture among the composites tested. In general, the plastic zone increased in size as the test temperature was increased. Introduction of fibers increased r_y' over that of the unfilled PPO, the extent of which appear to be independent of adhesion. In contrast, r_y of the glass bead composite was nearly the same as that of the polymer when adhesion was present but much greater than that of the polymer when no adhesion was present. A microscopic study of the region around the crack tip has been made. We find that there is no visibly well-defined plastic zone for the unfilled PPO, but rather a continuous increase in deformation intensity as one approaches the crack tip. The PPO composites, however, show surprisingly well-defined plastic zones, which correlate well with calculated r_y's. As crazing and/or debonding occurred in the composites, a refractive index change resulted which allowed photographs of the plastic zone to be taken without polarized light.

Figure 15 illustrates a typical plastic zone observed visually during testing of the glass fiber composites. Before a load is applied, the area around the crack tip is clear and homogeneous. During deformation the darkened area slowly grows, clearly defining the volume of irreversible changes within the material.

Figure 15 shows the zone after loading the sample to within 80% to 90% of the fracture load and subsequently releasing the load. Catastrophic failure eventually occurred from the notch with the larger plastic zone, since it reached the critical stress intensity before the other notched region.

Since photographs of the above type were not taken at the instant of fracture, the plastic zones measured from the pictures were usually somewhat lower than the r_y's that actually existed at break.

In Figure 16 measurements for the glass fiber composite plastic zones are compared to r_y at various temperatures. As seen, agreement is good. Similar results were obtained at other filler concentrations. The above photographic analysis gives support to the fact that r_y actually exists as an entity at the crack tip for polymeric composites.

(c) Discussion of Results

The fracture toughness can be written in the form:

$$\gamma = \pi \, r_y \sigma_y^2 (1 - \nu^2)/E$$

or since the Poisson ratio ν is usually about 0.35 and constant,

$$\gamma = 2.8 \, r_y \sigma_y^2 /E$$

The plane strain fracture toughness is thus a function of the deformation processes occurring at the crack tip and the bulk properties of the material.

The above equation for γ shows that the fracture resistance of composites which contain rigid fillers can be increased over that of the unfilled polymer by sufficiently increasing the crack tip plasticity and/or the yield (or ultimate) strength. For example, at 25°C the elastic modulus of the 20% by volume A-1100 treated glass fiber composite is approximately 3 times that of the unfilled PPO modulus. The composite plastic zone size and ultimate strength are nearly 1.6 and 1.8 times that of the unfilled PPO, respectively. As a result, the composite fracture toughness is 54% greater than that of the unfilled PPO. Listed in Table 1 are examples for each of the other composites at 25°C.

A performance chart for the PPO composites, based on mechanical properties, is shown in Table 2. Ordinarily, when modulus and strength of isotropic materials are increased, the material becomes more susceptible to brittle failure, as with hardened steels. This is not so for the quasi-isotropic fiber composites, as Table 2 shows. Although none of the composites investigated has a "clear cut" advantage over any of the others, the 20% by volume A-1100 glass fiber composite ranked first in overall performance, showing that with moderate adhesion between fiber and polymer, not only was the tensile strength and modulus significantly increased, but the fracture toughness was also improved. Presumably, increased adhesion can still cause further improvement, since the A-1100 promoted only a moderate degree of adhesion.

It is felt that these results present a strong case for further development and refinement of quasi-isotropic composite systems for use as structural materials.

ACKNOWLEDGMENT

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TABLE 1. RELATIVE VALUES OF γ FOR PPO COMPOSITES AT 25°C

MATERIAL	$\dfrac{r_y \text{ composite}}{r_y \text{ PPO}}$	$\dfrac{\sigma_y \text{ composite}}{\sigma_y \text{ PPO}}$	$\dfrac{E \text{ composite}}{E \text{ PPO}}$	$\dfrac{\gamma \text{ composite}}{\gamma \text{ PPO}}$
20% untreated glass bead composite	2.2	.76	1.5	.84
20% A-1100 treated glass bead composite	.80	.92	1.5	.45
20% untreated glass fiber composite	1.6	1.4	3.0	1.05
20% A-1100 treated glass fiber composite	1.8	1.6	3.0	1.54
20% graphite fiber composite	6.5	1.0	6.0	1.08
10% untreated glass fiber composite	1.6	1.1	1.8	1.08
30% untreated fiber composite	1.9	1.3	4.1	.78

TABLE 2   COMPOSITE PERFORMANCE CHART

Design For High→	Ultimate Strain ε_u	Ultimate Strength σ_u	Elastic Modulus E	Fracture Resistance γ
Unfilled PPO	1*	4	6	2
20%/vol Glass Bead Composite	2	6	5	?
20%/vol A-1100 Glass Bead Composite	3	5	5	3
20%/vol Glass Fiber Composite	5	2	2	2
20%/vol A-1100 Glass Fiber Composite	4	1	2	1
20%/vol Graphite Fiber Composite	6	3	1	2

* 1 Is The Highest Rating

LIST OF FIGURES

FIGURE 1. SAMPLE GEOMETRY FOR FRACTURE TOUGHNESS TEST
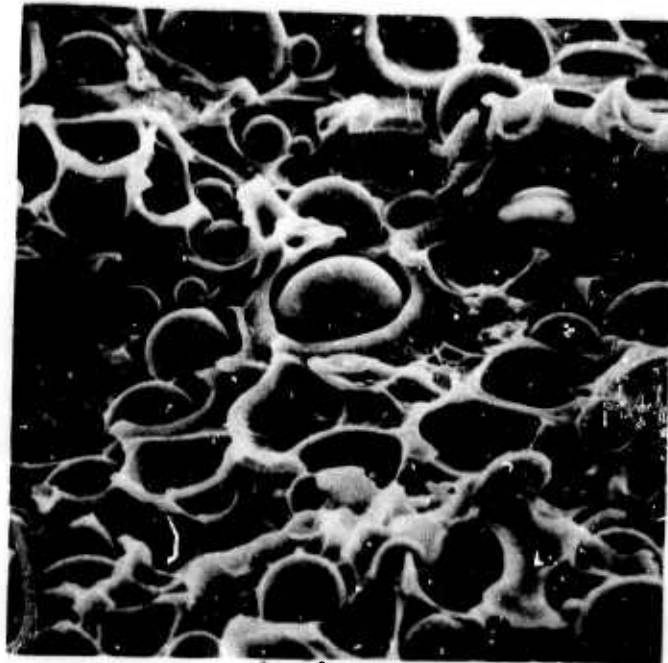
|←→| .001 cm

Electron Scanning Photograph 20%/Vol
Untreated Glass Bead/PPO Composite
Fast Crack Region

FIGURE 2. FRACTURE SURFACE OF AN UNTREATED GLASS BEAD/PPO COMPOSITE AT 25°C

.001 cm
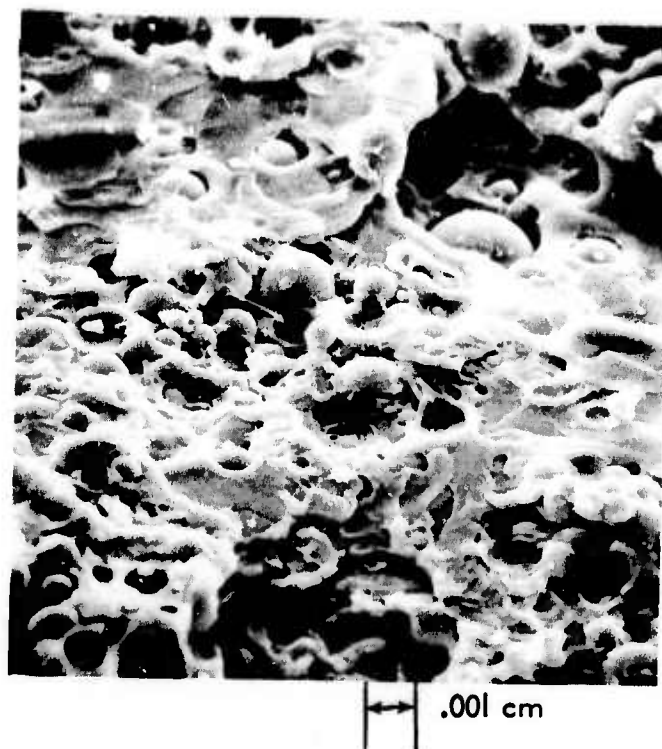
20%/Vol A-1100 Glass Bead/PPO Composite
Fast Crack Region

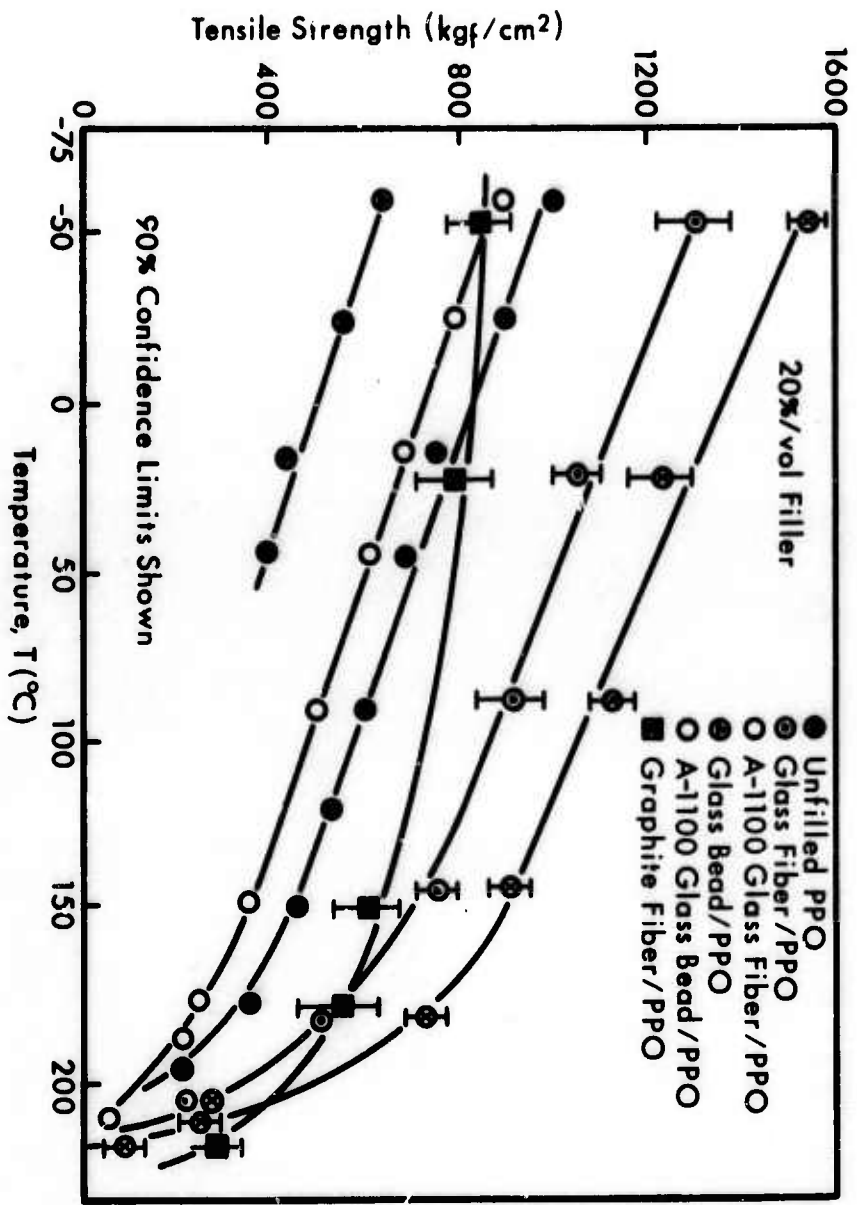FIGURE 3. FRACTURE SURFACE OF A BEAD COMPOSITE WITH ADHESION

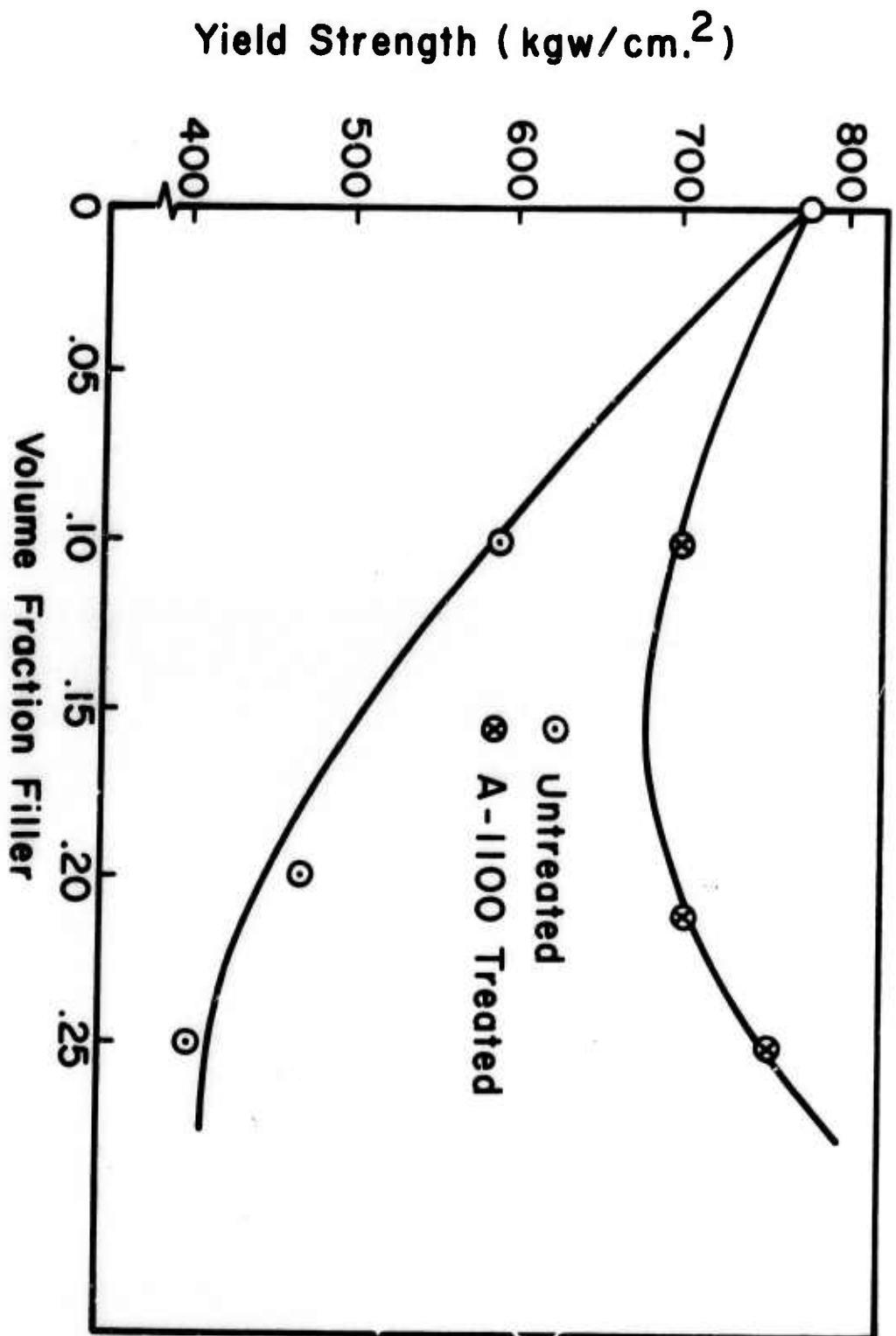FIGURE 4. EFFECT OF TEMPERATURE ON COMPOSITE TENSILE STRENGTH
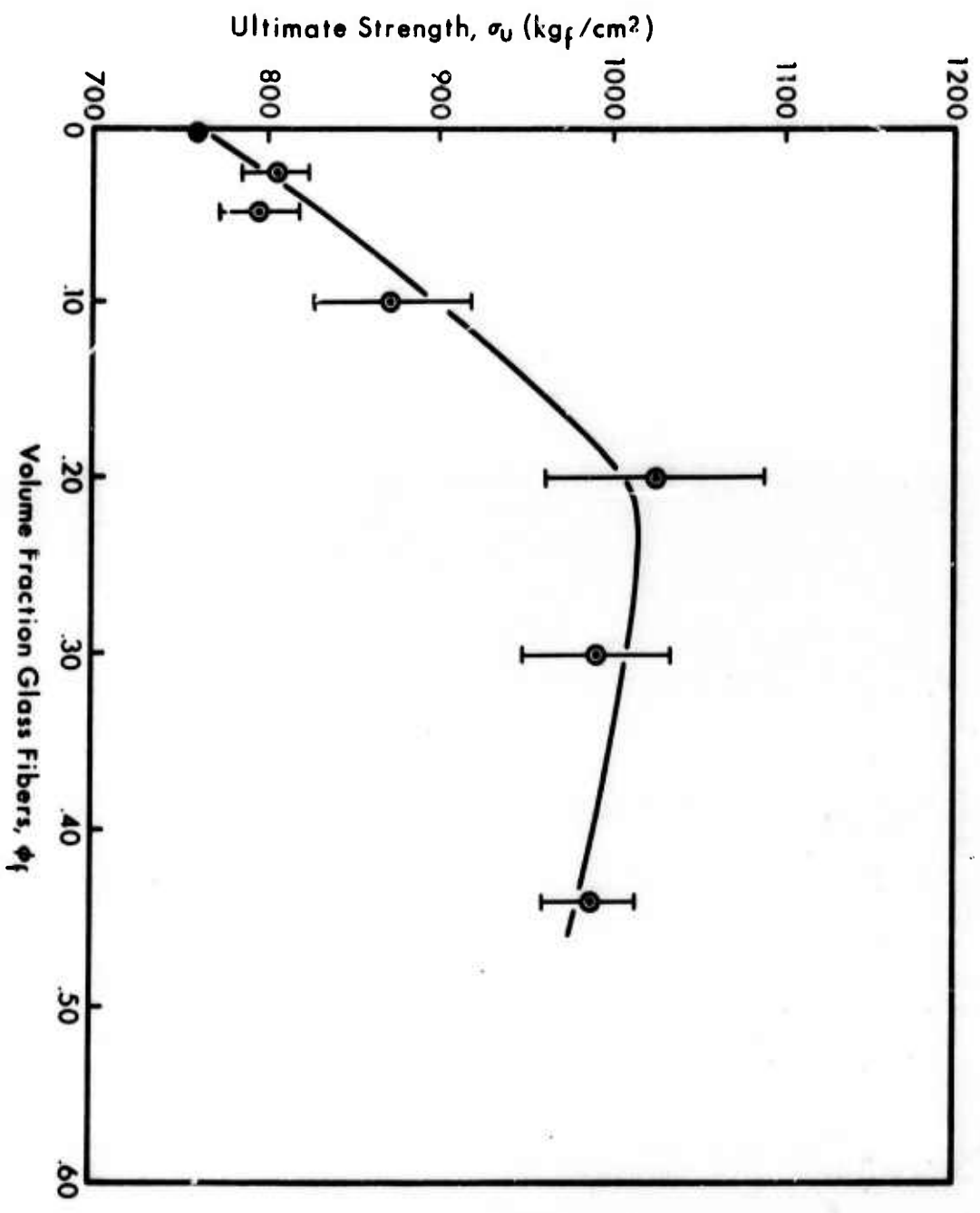
FIGURE 5. EFFECT OF SURFACE TREATMENT ON STRENGTH OF GLASS BEAD/PPO COMPOSITES

FIGURE 6. EFFECT OF FILLER CONTENT ON GLASS FIBER COMPOSITE TENSILE STRENGTH
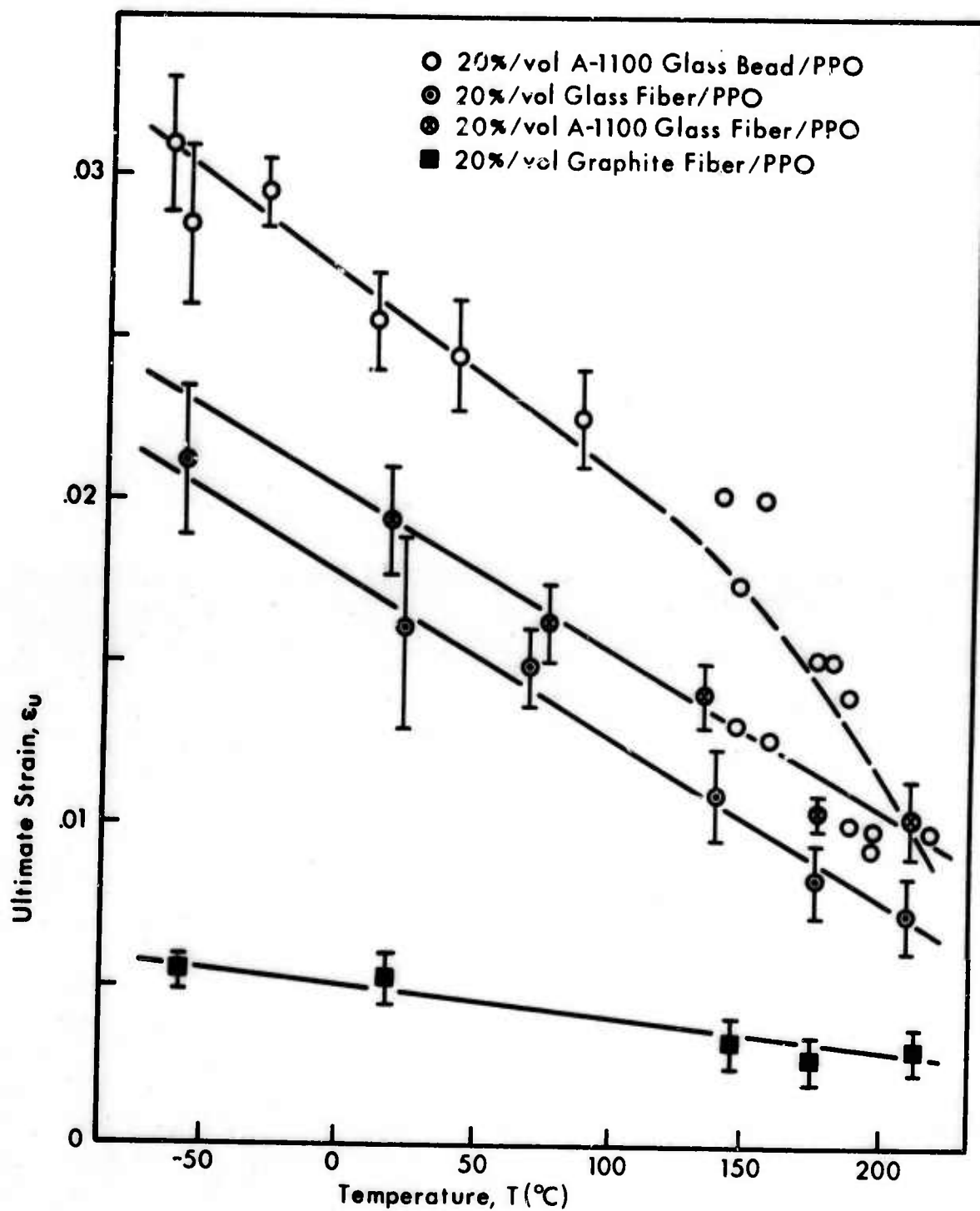
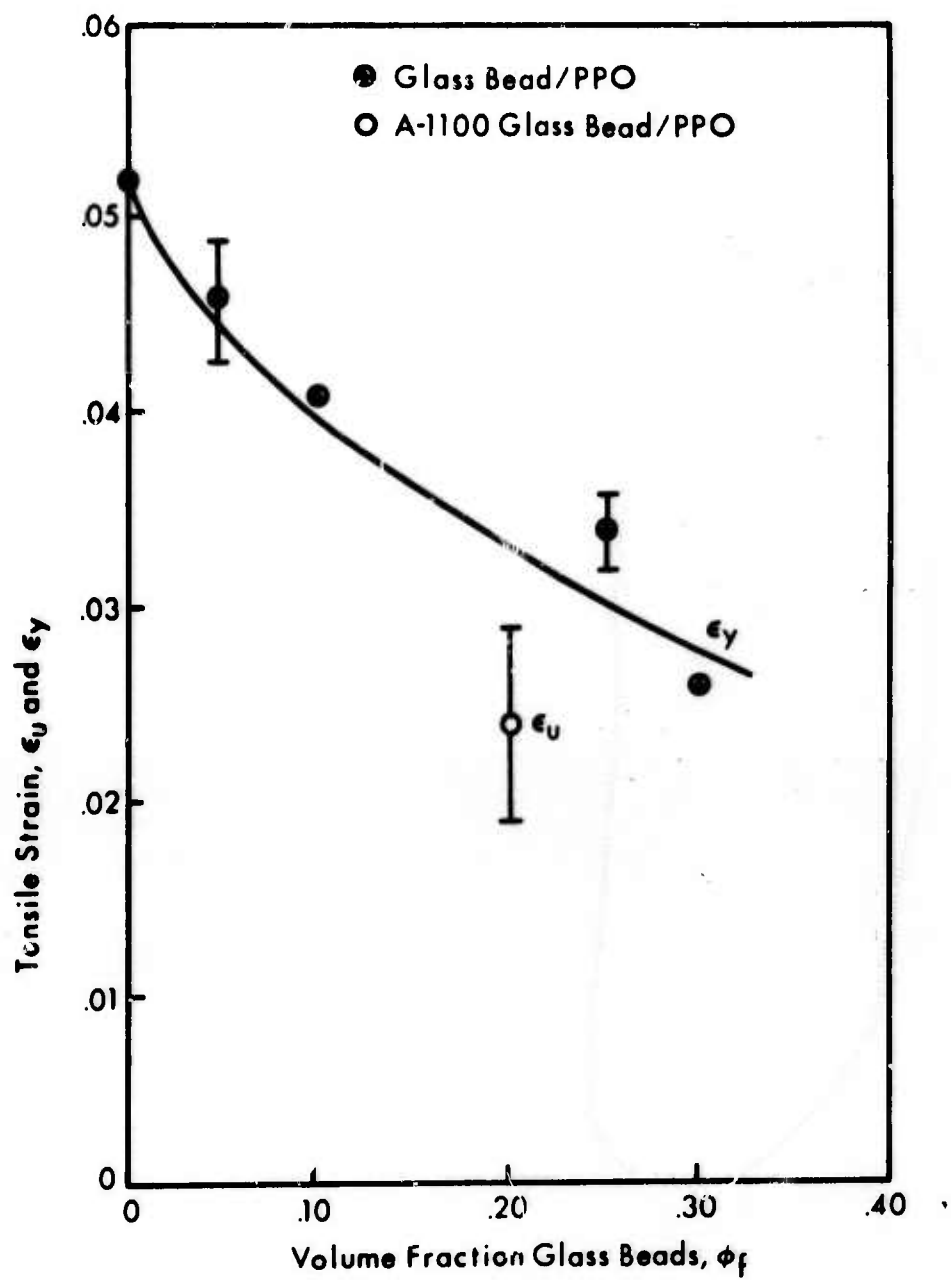FIGURE 7. EFFECT OF TEMPERATURE ON COMPOSITE TENSILE STRAIN

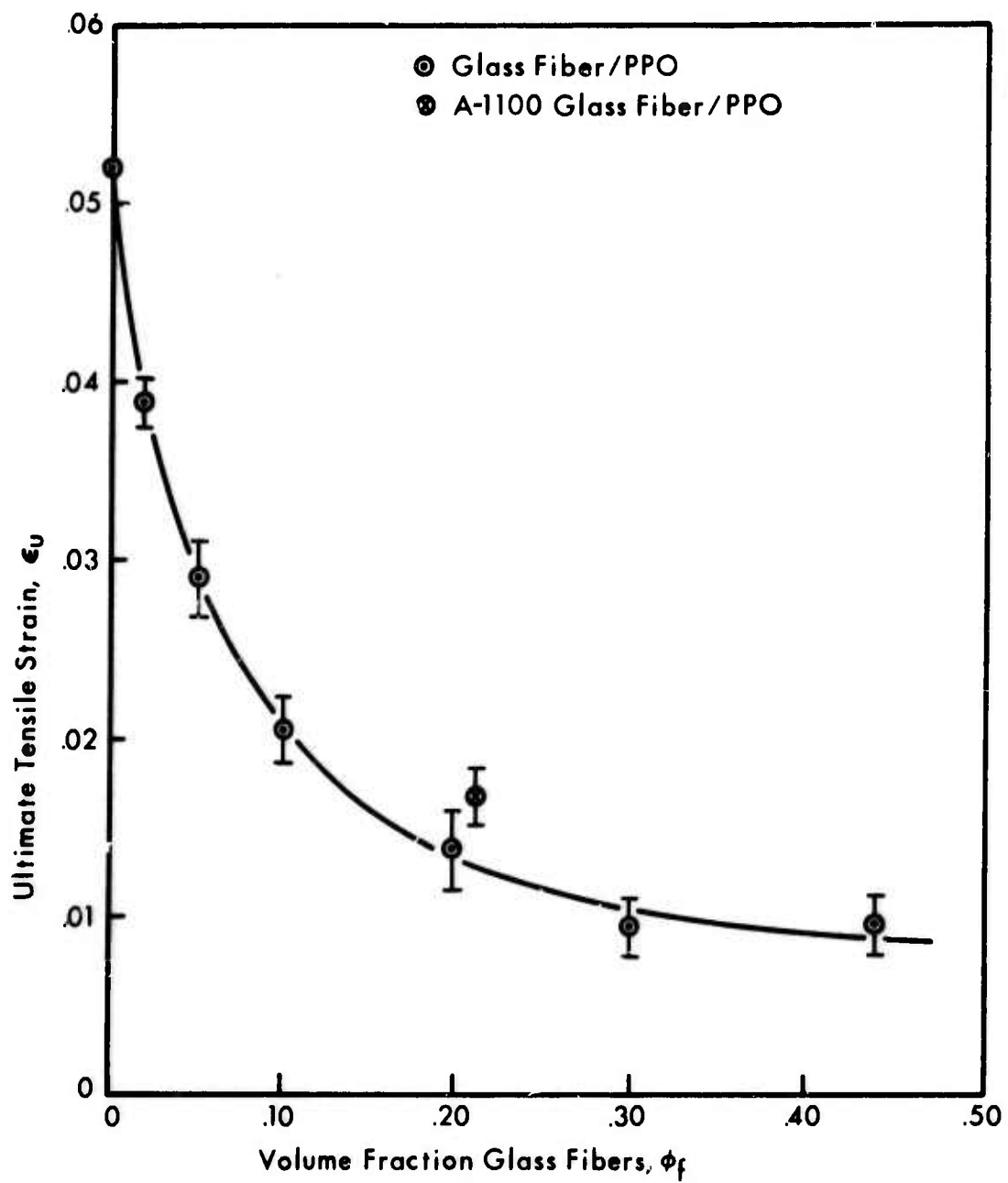FIGURE 8. EFFECT OF FILLER CONTENT ON GLASS BEAD COMPOSITE TENSILE STRAIN

FIGURE 9.   EFFECT OF FILLER CONTENT ON GLASS FIBER COMPOSITE
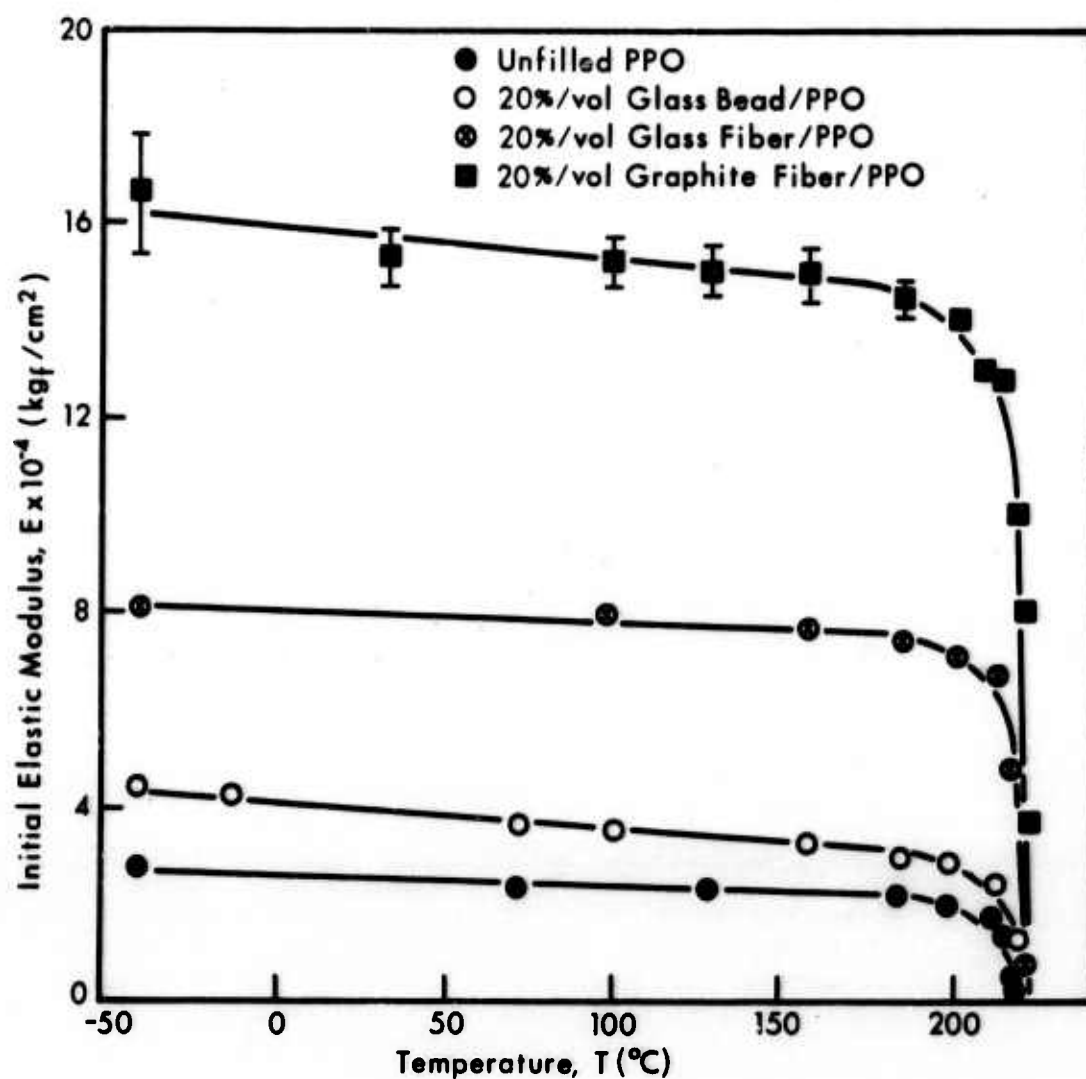ULTIMATE TENSILE STRAIN

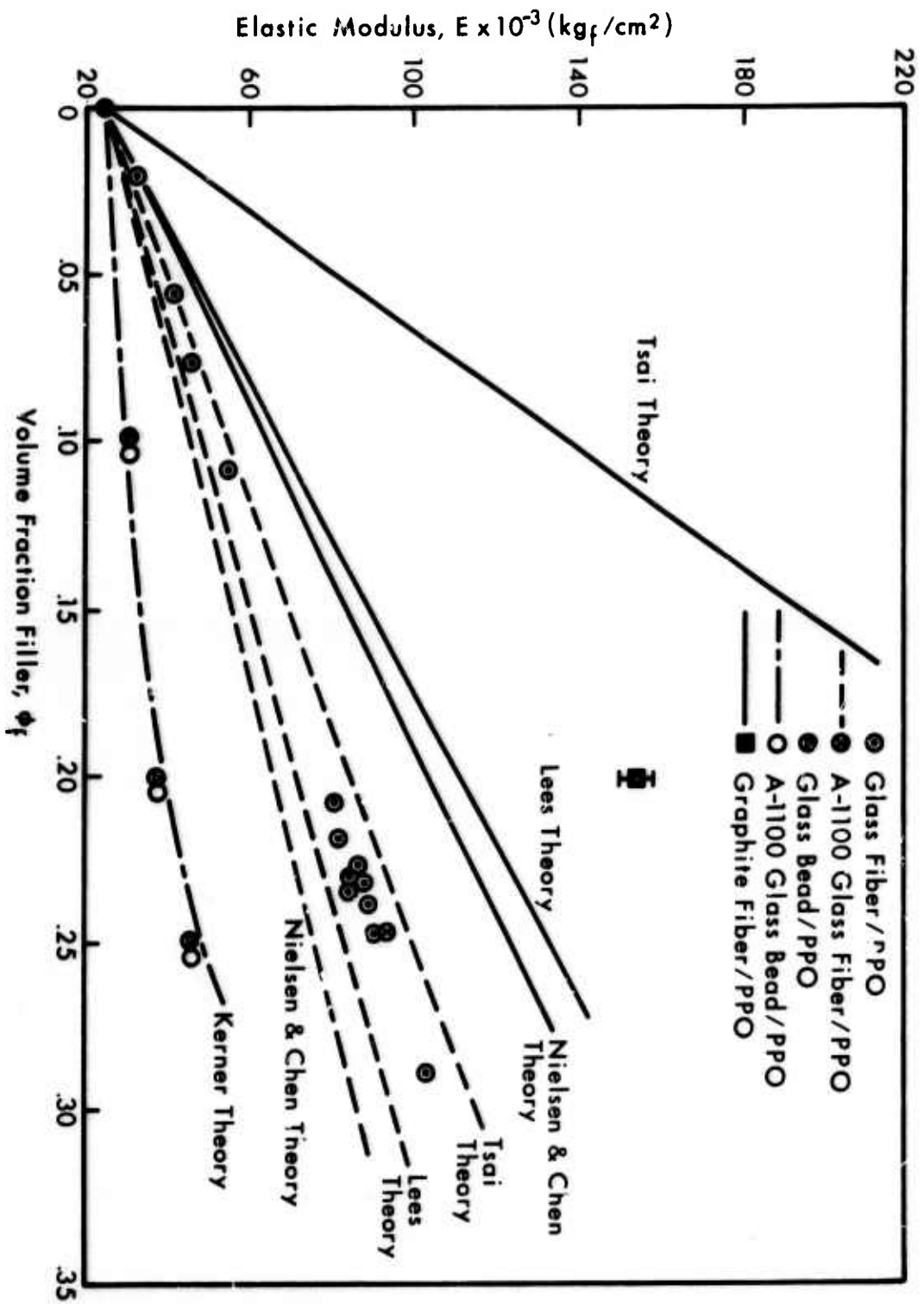FIGURE 10. EFFECT OF TEMPERATURE ON COMPOSITE INITIAL ELASTIC MODULUS

FIGURE II. EFFECT OF FILLER CONTENT ON COMPOSITE INITIAL ELASTIC MODULUS

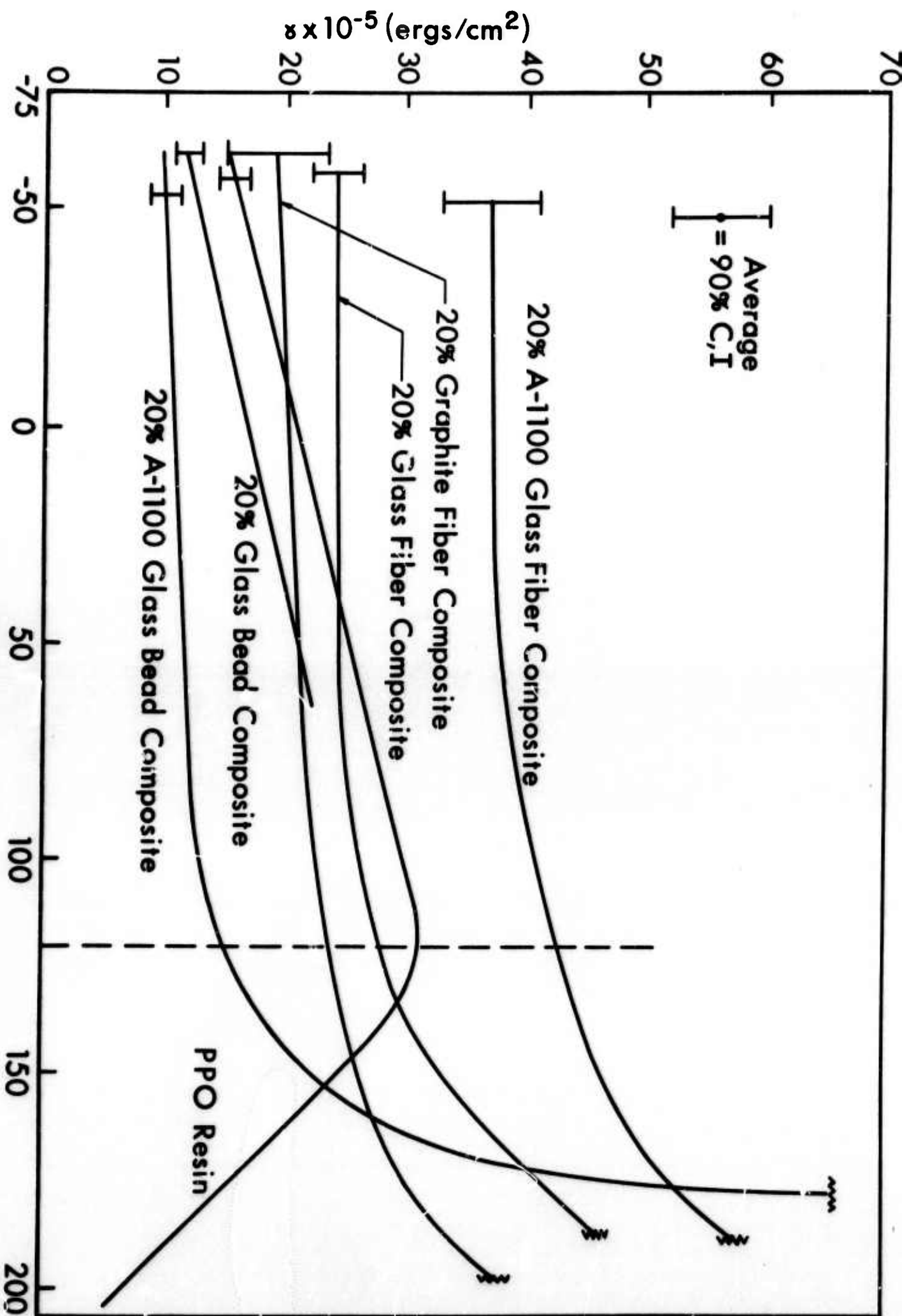Figure 12. THE FRACTURE TOUGHNESS OF PPO COMPOSITES.

$\gamma \times 10^{-5} \, (\text{ergs/cm}^2)$

Volume Fraction Filler, Φ_f

◎ Glass Fiber/PPO
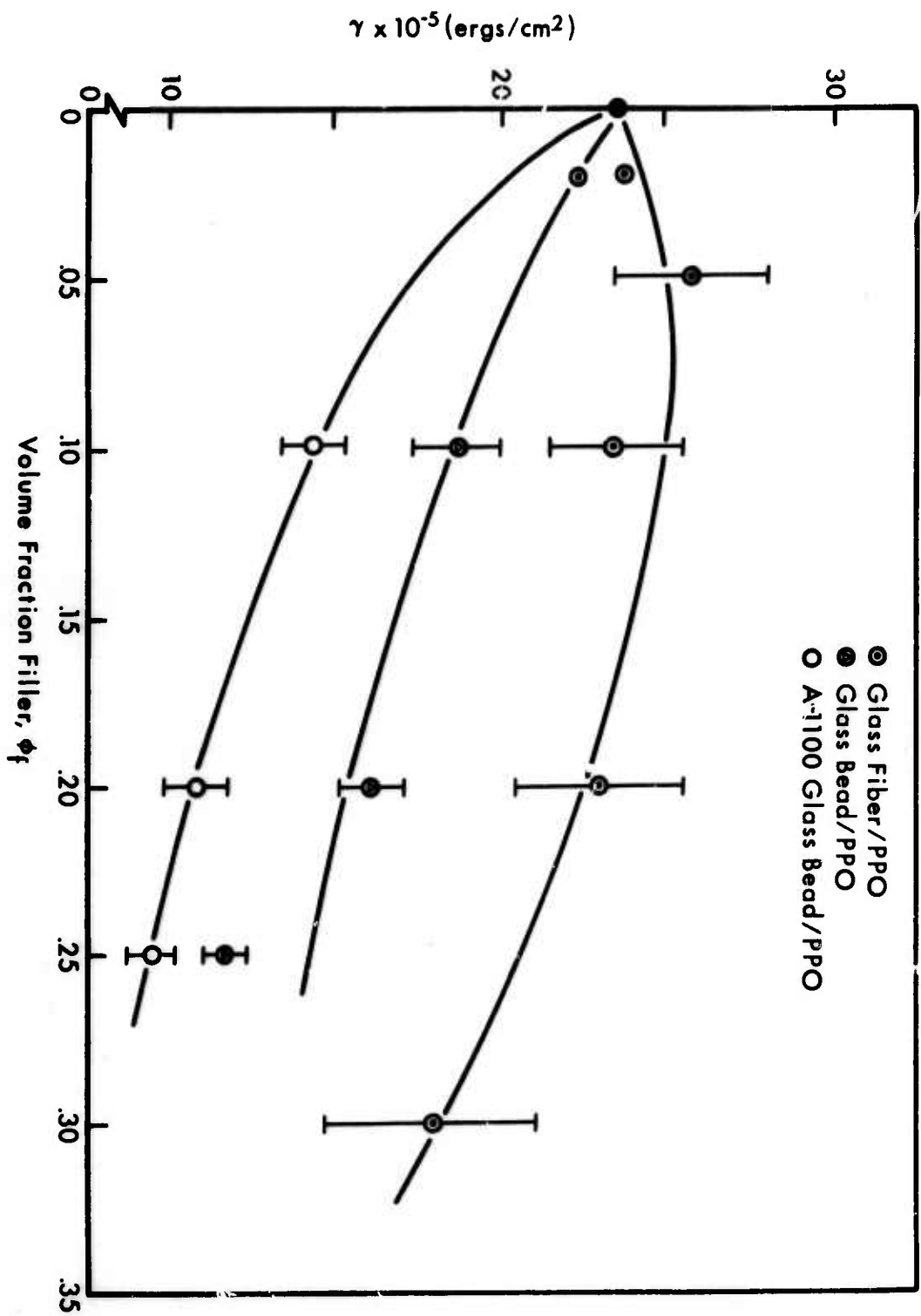● Glass Bead/PPO
○ A-1100 Glass Bead/PPO

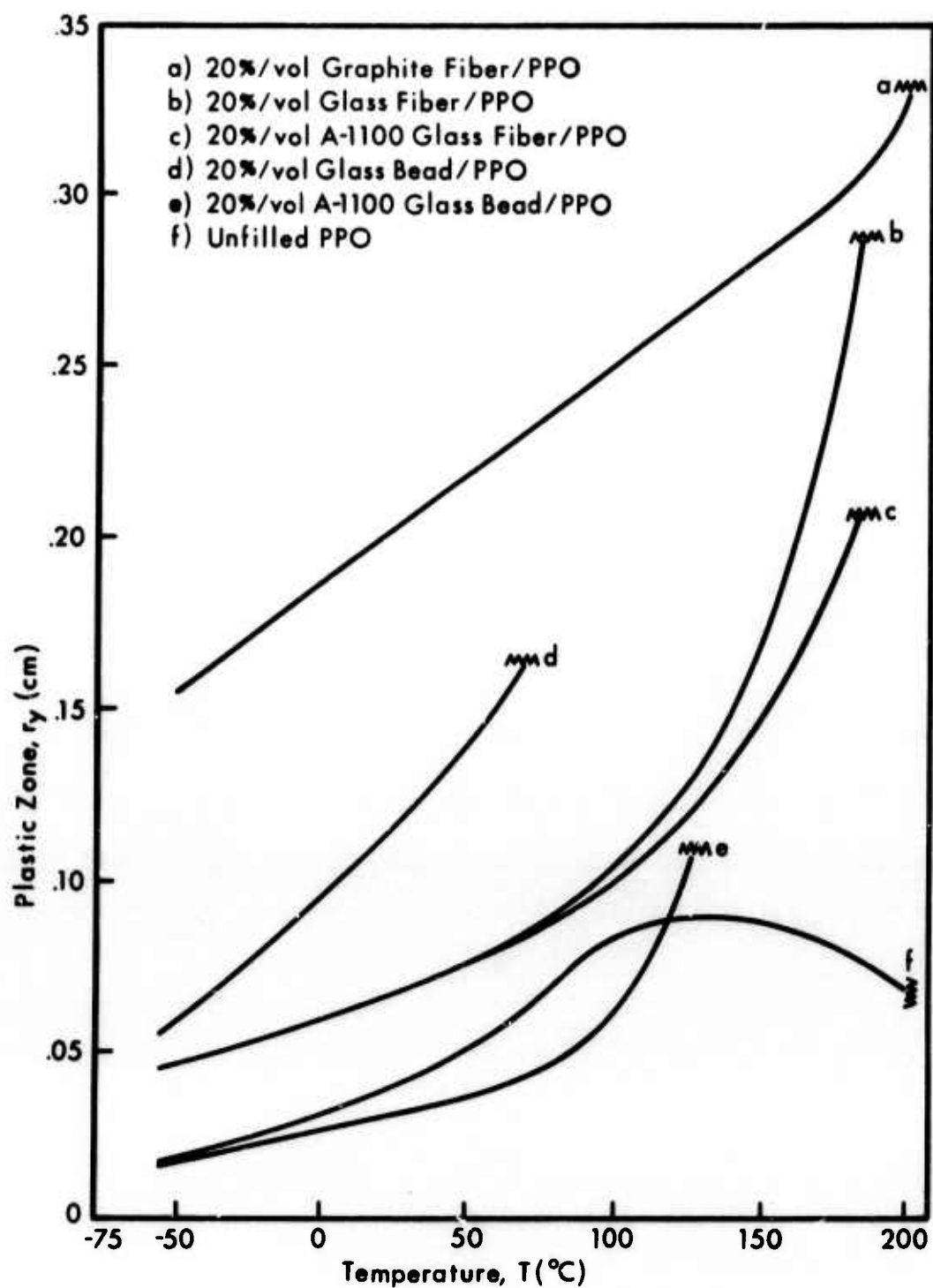FIGURE 13. EFFECT OF FILLER CONTENT ON COMPOSITE FRACTURE ENERGY AT 20°C

FIGURE 14. EFFECT OF TEMPERATURE ON THE COMPOSITE PLASTIC ZONE CALCULATED
FROM IRWIN'S FRACTURE MECHANICS

Optical Transmission

20%/Vol Untreated Glass Fiber Composite

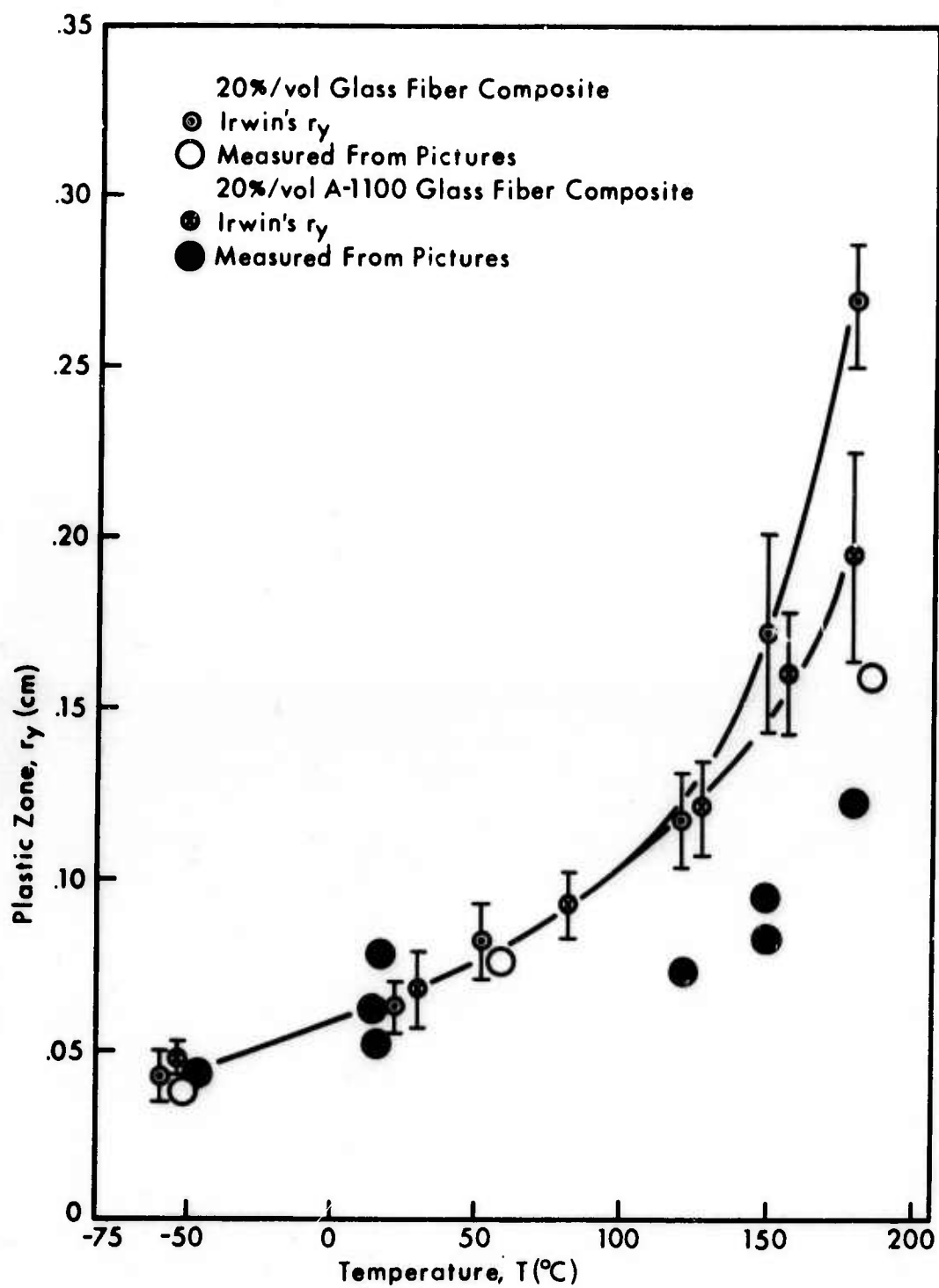FIGURE 15. PLASTIC ZONE SIZES AT THE NOTCHES IN A GLASS FIBER COMPOSITE
AT 350°F

FIGURE 16.   COMPARISON OF CALCULATED AND MEASURED VALUES
OF GLASS FIBER COMPOSITE PLASTIC ZONES

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13. ABSTRACT

The mechanical properties of glass bead, randomly oriented short glass fiber and randomly oriented short graphite fiber polyphenylene oxide composites were investigated. Fracture toughness measurements were made using double edge notched tensile specimens and tensile strength, tensile strain and initial elastic modulus were measured in standard ASTM tensile tests.

It was found that the fracture toughness was relatively independent of filler types and geometry (and nearly equal to that of the unfilled polymer) when no polymer-filler adhesion was present. When adhesion was promoted by surface treatment of the reinforcement, the fracture toughness of the treated fiber composites was greater than that of the untreated composites, while that of the treated particulate composites was below that of the untreated materials. The fracture toughness was also relatively independent of fiber concentration, but decreased sharply with increased glass bead concentration.

The elastic moduli of the composites varied in a predictable fashion with temperature and reinforcement concentration. The ultimate tensile strength and the elongation at break were a sensitive function of interfacial adhesion and reinforcement geometry. The overall performance of the various systems was evaluated by considering the combined mechanical response of each system and rating them relative to one another.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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glass beads						
random fiber orientation						
quasi isotropic						
mechanical properties						
tensile strength						
tensile modulus						
tensile strain						
fracture toughness						
plastic zone						
adhesion						
electron scanning micrographs						
temperature						